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Shape of the R and P lines in the fundamental band of gaseous HD

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Within the classical path impact formalism, theoretical expressions are derived for the line shape and intensity of the R and P lines of the fundamental band of gaseous HD. These reflect the interplay between the allowed dipole moment and the dipole moments induced during binary collisions. The interference between the allowed and the induced dipoles and between the dipoles induced in different collisions lead to a line shape which is a superposition of a Lorentzian and an anomalous dispersion profile in agreement with experiment.

I. INTRODUCTION

The fundamental absorption band of gaseous HD was first observed by Durie and Herzberg.[1] More recently, this band has been studied by McKellar,[2,3] Bejar and Gush,[4] and Prasad and Reddy.[5] The shapes as well as the intensities of the R and P lines were investigated by McKellar as a function of the density at 77 K.[2] He found that the experimental profiles could be well represented at a given density by a Fano profile; that is, by the sum of a Lorentzian and an anomalous dispersion line shape.

The theoretical shape of the R and P lines, which is the subject of the present paper, results from a subtle interplay between the weak permanent dipole moment, $\vec{\mu}^A$, of an absorbing molecule and the dipole moment, $\vec{\mu}^I$, induced during binary collisions. By itself, the permanent dipole moment gives rise to pressure-broadened R and P lines with widths, Γ, and intensities proportional to the density, n. The majority of the absorption arising from the induced dipole moments appears as very broad asymmetric features proportional to n^2. Their breadth is due to the fact that the induced absorption takes place only during collisions and not in between. Therefore, the ratio of the width of a pure allowed to that of a pure induced line is quite small and of order $\tau_d\Gamma$, where τ_d denotes the duration of a collision and Γ is the width in angular frequency units. We will not concern ourselves with these broad features in the present paper, as they have been discussed extensively in the literature[6]; furthermore, in high resolution these lines would appear as a broad background on which the sharp lines sit.

When permanent and induced dipoles are both present, interference between these can take place.[7-9] This interference is proportional to the product of the matrix elements $\vec{\mu}^A_{if}$ and $\vec{\mu}^I_{if}$, and varies quadratically with the density. The importance of the interference as compared to the allowed intensity, depends on the ratio $\vec{\mu}^I_{if}\,\zeta/\vec{\mu}^A_{if}$; here ζ is a dimensionless parameter given by $\zeta = n\sigma^3 = \tau_d/\tau_c$, where σ is the molecular diameter, and τ_c denotes the time between collisions. In contrast to most polar molecules for which the transition dipoles are relatively large, HD has an unusually small fundamental allowed dipole matrix element ($\approx 5 \times 10^{-5}$ D). Because the corresponding induced transition moments are typically of order 10^{-2} D, the interference in HD is important for densities $n > 10$ amagat. Also, because the interference is proportional to the allowed matrix element, the corresponding contribution to the absorption spectrum is sharp, and it modifies both the spectral line shape and intensity. The modification of the intensity of the HD lines was considered previously under the assumption of uncoupled internal and translational motions.[8] It was found that, in qualitative agreement with experiment, the intensity decreased linearly at approximately 1%/amagat. In addition to the interference discussed above, there is another interference of consequence at high densities due to the correlation between pure induced dipoles in subsequent binary collisions.[9] This effect, which varies as n^3, also modifies both the line shape and intensity of the shape lines. (This was referred to as "constructive intercollisional interference" in Ref. 9.)

In the present paper we shall discuss the shape of the fundamental R and P lines using the classical path and the impact approximations.[10] In Sec. II we first introduce the appropriate dipole cor-

relation functions and review their relation to the line shape. In the following three sections, we then treat the pressure-broadened allowed spectrum, the interference effect between the allowed and the induced dipole moments, and the sharp interference associated with the induced dipoles, respectively. In the final section, after considering several limiting cases which illustrate the qualitative behavior of the interference effects, we compare our results with the experimental results of McKellar.[2]

II. DIPOLE CORRELATION FUNCTIONS

As is well known, the absorption coefficient is related to the Fourier transform of the dipole autocorrelation function. In the following sections, we will perform the calculations as if only one of the molecules, referred to as the absorbing molecule, can absorb radiation and multiply the resulting absorption coefficient by the total number of molecules, N. In this picture all other molecules will be referred to as perturbers. The absorption coefficient per unit wavelength at frequency ω, $\alpha(\omega)$, can therefore be written in the form

$$\alpha(\omega) = n(4\pi^2/3\hbar c)\omega(1 - e^{-\beta\hbar\omega})\phi(\omega), \tag{1}$$

where the line-shape function $\phi(\omega)$ is given by

$$\phi(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\omega t}C(t)dt \tag{2}$$

and the corresponding dipole correlation function $C(t)$ is

$$C(t) = \langle\vec{\mu}(0)\cdot\vec{\mu}(t)\rangle. \tag{3}$$

The angular brackets denote an ensemble average and the other symbols have their standard meaning. For the fundamental band, the stimulated emission factor $e^{-\beta\hbar\omega}$ is negligible. The correlation function $C(t)$ satisfies the symmetry relation

$$C(-t) = C(t)^* \tag{4}$$

and the line-shape function can accordingly be written as a real function

$$\phi(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^{\infty} e^{-i\omega t}C(t)dt\,. \tag{5}$$

The dipole moment operator $\vec{\mu}(t)$ occurring in (3) is a Heisenberg operator and in the present case can be represented by

$$\vec{\mu}(t) = \vec{\mu}^A(t) + \sum_j \vec{\mu}_j^I(t), \tag{6}$$

where $\vec{\mu}^A(t)$ is the allowed dipole of the absorbing molecule, and $\vec{\mu}_j^I(t)$ is the dipole induced in a collision between the absorber and the perturber j. Using (6), the correlation function $C(t)$ can be written as a sum of n-body contributions, $C_n(t)$; specifically,

$$C(t) = C_1^{AA}(t) + C_2^{AI}(t) + C_2^{IA}(t) + C_3^{II}(t). \tag{7}$$

In this expression

$$C_1^{AA}(t) = \langle\vec{\mu}^A(0)\cdot\vec{\mu}^A(t)\rangle, \tag{8}$$

$$C_2^{AI}(t) = \left\langle\vec{\mu}^A(0)\cdot\sum_j\vec{\mu}_j^I(t)\right\rangle = N\langle\vec{\mu}^A(0)\cdot\vec{\mu}^I(t)\rangle, \tag{9}$$

$$C_2^{IA}(t) = \left\langle\sum_j\vec{\mu}_j^I(0)\cdot\vec{\mu}^A(t)\right\rangle = N\langle\vec{\mu}^I(0)\cdot\vec{\mu}^A(t)\rangle, \tag{10}$$

and

$$C_3^{II}(t) = \left\langle\sum_j\vec{\mu}_j^I(0)\cdot\sum_{k\neq j}\vec{\mu}_k^I(t)\right\rangle = N^2\langle\vec{\mu}_1^I(0)\cdot\vec{\mu}_2^I(t)\rangle, \tag{11}$$

where $\vec{\mu}_1^I$ and $\vec{\mu}_2^I$ refer to two different perturbers. In writing Eq. (7), we have neglected the two-body induced dipole correlation function

$$C_2^{II}(t) = N\langle\vec{\mu}_1^I(0)\cdot\vec{\mu}_1^I(t)\rangle,$$

for the reasons discussed in the Introduction. In addition, we will not consider the correlations between the allowed dipoles associated with different absorbers, which are expected to be small in the present case. The one-, two-, and three-body contributions will be considered in the following three sections, respectively.

III. PURE ALLOWED SPECTRUM

In this section we review the well-known results for the shape of an isolated pressure broadened spectral line.[11] The theory is based on the classical path approximation[12] in which the density matrix is written as a product of absorber and perturber density matrices, and in which the translational motion is treated classically. The effect of the translation on the internal degrees of freedom of the absorbing molecule is described by a time-dependent potential. Within the approximation, the dipole correlation function can be written[10]

$$C_1^{AA}(t) = \sum_{if}\rho_{ii}\{\vec{\mu}_{if}^A(0)\cdot\vec{\mu}_{fi}^A(t)\}, \tag{12}$$

where ρ denotes the absorber density matrix and i and f refer to the substates associated with the initial and final energy levels, respectively. The curly brackets refers to a classical ensemble average over the translational motion. With the additional assumption of well-separated lines, Eq. (12) can be written in the form

$$C_1^{AA}(t) = \sum_{if} \rho_{ii} |\vec{\mu}^A_{if}|^2 \sum_{i'f'} e^{i\omega^0_{f'i'}t} \{U^*_{f'f}(t) U_{i'i}(t)\}$$

$$= \sum_{if} \rho_{ii} |\vec{\mu}^A_{if}|^2 \sum_{i'f'} e^{i\omega^0_{f'i'}t} \langle\langle i'f' | \{U_i(t) U^\dagger_f(t)\} | if\rangle\rangle \tag{13}$$

using line-space notation[13]; U denotes the time-evolution operator of the internal states of the absorber in the interaction representation, and ω^0_{fi} is the unperturbed transition frequency.

We use the standard impact theory to evaluate (13). In this approximation all collisions are treated as statistically independent. In addition, the actual radiation dipole matrix elements during a collision are replaced by those which would have occurred during an instantaneous collision with the same overall phase shift. Hence, the actual allowed dipole is misrepresented during a fraction τ_d/τ_c of its time history; for $\tau_d/\tau_c \ll 1$ this does not give rise to appreciable error, however. With these assumptions the line-space matrix element in (13) is given by[10]

$$\langle\langle i'f' | \{U_i(t) U_f(t)^\dagger\} | if\rangle\rangle = \delta_{ii'}\delta_{ff'} e^{-\Gamma_{fi}t/2}. \tag{14}$$

The quantity Γ_{fi} is in general complex, $\Gamma_{fi} = \Gamma'_{fi} + i\Gamma''_{fi}$, and can in principle be calculated from the time-dependent interaction potential.[11] In this paper we are interested in the $R(J)$ and $P(J)$ lines of the fundamental band, and performing the sum over all substates in this case, we finally obtain for the correlation function

$$C_1^{AA}(t) = P(J) |m| (p^A_{JJ'})^2 e^{i\omega_{J'J}t - \Gamma'_{J'J}t/2}, \tag{15}$$

where $p^A_{JJ'}$ is the transition dipole strength,[8]

$$\omega_{J'J} = \omega^0_{J'J} - \tfrac{1}{2}\Gamma''_{J'J},$$

$|m|$ is $J+1$ for R and J for P lines, and $P(J)$ is the Boltzmann function for the initial state normalized according to $\sum_J (2J+1)P(J) = 1$.

The correlation function (15) yields a symmetric Lorentzian line shape

$$\phi^{AA}(\omega) = P(J) |m| (p^A_{JJ'})^2 \frac{\Gamma'_{J'J}/2\pi}{(\frac{1}{2}\Gamma'_{J'J})^2 + (\omega - \omega_{J'J})^2} \tag{16}$$

which is characterized by the width $\Gamma'_{J'J}$ and the shifted center frequency $\omega_{J'J}$. The corresponding intensities $\int \alpha(\omega) d\omega/\omega$ which are independent of the broadening and shifting, can be obtained either by integrating over the line-shape function or from the correlation function [Eq. (15)] at $t = 0$.

IV. INTERFERENCE BETWEEN ALLOWED AND INDUCED DIPOLES

In this section we will consider the two-body correlations C_2^{AI} and C_2^{IA} which describe the interference between the allowed and the induced dipoles. As pointed out in the Introduction, this interference will be important if $(\vec{\mu}^I_{if}\tau_d)/(\vec{\mu}^A_{if}\tau_c)$ is of order unity. In the classical path approximation $C_2^{AI}(t)$ becomes

$$C_2^{AI}(t) = N \sum_{if} \rho_{ii} \{\vec{\mu}^A_{if}(0) \cdot \vec{\mu}^I_{fi}(t; \vec{R}(t))\}, \tag{17}$$

where the time dependence of the induced dipole matrix element is due to two sources. In the first place, the internal states of the absorber change under the influence of the time-dependent forces exerted by the perturbers as before. In the second place, the induced dipole has an explicit dependence on the absorber-perturber separation $\vec{R}$ which, in the classical path approximation, is a definite function of time. For a nonzero contribution to $C_2^{AI}(t)$, it is necessary that both $\vec{\mu}^A$ and $\vec{\mu}^I$ have nonvanishing matrix elements between the same initial and final states i and f. As discussed in detail previously,[8,9] the only component of $\vec{\mu}^I$ which satisfies this requirement is of the form

$$\vec{\mu}^I_{if}(t; \vec{R}(t)) = \vec{\mu}^A_{if}(t) p(R(t)), \tag{18}$$

where $p(R)$ represents the strength of the induced dipole. Again, for well-separated lines, we have in analogy with (13)

$$C_2^{AI}(t) = N \sum_{if} \rho_{ii} |\vec{\mu}^A_{if}|^2 \sum_{i'f'} e^{i\omega^0_{f'i'}t} \langle\langle i'f' | \{p(R(t)) U_i(t) U^\dagger_f(t)\} | if\rangle\rangle . \tag{19}$$

Note that $C_2^{AI}(0)$, which is related to the integrated intensity, is given by

$$C_2^{AI}(0) = N \sum_{if} \rho_{ii} |\vec{\mu}^A_{if}|^2 \{p(R)\}$$

$$= nP(J) |m| (p^A_{JJ'})^2 4\pi \int_0^\infty p(R) g(R) R^2 \, dR . \tag{20}$$

We now discuss the quantity

$$\{p(R(t)) U_i(t) U^\dagger_f(t)\}$$

in the impact approximation. For statistically independent collisions we can write

$$\{p(R(t)) U_i(t) U^\dagger_f(t)\}$$

$$= \{U_i(t - \tau_d) U^\dagger_f(t - \tau_d)\} \{p(R(t)) U_i(\tau_d) U^\dagger_f(\tau_d)\}. \tag{21}$$

The first factor on the right-hand side of Eq. (21) describes the evolution of the system from time zero to $t - \tau_d$; for $t \gg \tau_d$, this line-space matrix

element can be written as in the previous section

$$\langle\langle i'f' | \{U_i(t-\tau_d)U_f^\dagger(t-\tau_d)\} | if\rangle\rangle = \delta_{ii'}\delta_{ff'}e^{-\Gamma_{fi}t/2}\,. \tag{22}$$

For the second factor, where $U(\tau_d)$ denotes the time-evolution operator of the system from $t-\tau_d$ to t, we can write

$$\langle\langle i'f' | \{p(R(t))U_i(\tau_d)U_f^\dagger(\tau_d)\} | if\rangle\rangle = \delta_{ii'}\delta_{ff'}(p_{\rm av})_{if}\,, \tag{23}$$

where $(p_{\rm av})_{if}$ will be discussed in Sec. VI. Note that this average involves only single collisions, is in general complex, and for $t \gg \tau_d$ is independent of time. For comparison with the previous work,[8,9] it is convenient to introduce the complex quantity Δ_{if} defined by

$$(p_{\rm av})_{if} \equiv \Delta_{if}\frac{4\pi}{V}\int_0^\infty p(R)g(R)R^2\,dR = \Delta_{if}\{p(R)\}\,, \tag{24}$$

where $g(R)$ is the pair distribution function and V is the volume of the gas. After summing over substates we obtain for $C_2^{AI}(t)$

$$C_2^{AI}(t) = nP(J)|m|(p^A_{JJ'})^2 e^{i\omega_{J'J}t - \Gamma'_{J'J}t/2} \times \left(\Delta_{JJ'}4\pi\int_0^\infty p(R)g(R)R^2\,dR\right). \tag{25}$$

By a similar procedure, one can evaluate $C_2^{IA}(t)$; it turns out that $C_2^{AI}(t) = C_2^{IA}(t)$. Because Δ_{if} is complex, the total line-shape function associated with the interference between allowed and induced dipoles becomes a sum of a symmetric Lorentzian and an antisymmetric anomalous dispersion line shape, i.e.,

$$\phi^{AI}(\omega) + \phi^{IA}(\omega) = 2nP(J)|m|(p^A_{JJ'})^2 4\pi\int_0^\infty p(R)g(R)R^2\,dR \times\left(\frac{\Delta'_{J'J}\Gamma'_{J'J}/2\pi}{(\frac{1}{2}\Gamma'_{J'J})^2+(\omega-\omega_{J'J})^2} + \frac{\Delta''_{J'J}(\omega-\omega_{J'J})/\pi}{(\frac{1}{2}\Gamma'_{J'J})^2+(\omega-\omega_{J'J})^2}\right). \tag{26}$$

The anomalous dispersion component, which significantly alters the line shape, does not affect the integrated intensity. The integrated intensity due to the interference between the allowed and induced dipoles can be obtained directly from Eq. (20) (i.e., within the classical path formalism but without invoking the impact approximations), and it agrees with that found previously, calculated under the assumption of uncoupled translational and rotational motions.[8] This differs, however, from that obtained by integrating the line shape given above by the factor $\Delta'_{J'J}$. This difference arises because the impact approximation used to derive Eq. (26) is only valid for $t \gg \tau_d$. Thus, the line shape, while it provides a good approximation for several half-widths around the center of the line, is not correct in the far wings where it is well known that the impact shape can not apply. When comparing with experiment, however, it is appropriate to use Eq. (26), as will be discussed in detail in Sec. VI.

V. PURE INDUCED SPECTRUM

The two-body autocorrelation function of the induced dipole operator is responsible for the broad asymmetric absorption features proportional to n^2 which characterize collision-induced spectra.[6] In addition, for homonuclear molecules (notably H_2) the correlation between dipoles induced in different collisions leads to a destructive interference which is manifested by a sharp dip centered at the transition frequency.[14] In HD the induced dipole has additional components with symmetries such that the selection rules $\Delta J = \pm 1, \pm 3$, etc., are satisfied. These components induced in different collisions will interfere constructively[9] and lead to modifications of the shape and intensity of the R and P lines proportional to n^3. This interference can be treated within the present theoretical framework by a straightforward generalization of the results of Sec. IV.

Within the classical path impact formalism, the correlation function describing the pure induced dipole interference, $C_3^{II}(t)$, is given by

$$C_3^{II}(t) = N^2\sum_{if}\rho_{ii}\{\vec{\mu}^I_{if}(0;\vec{R}_1(0))\cdot\vec{\mu}^I_{fi}(t;\vec{R}_2(t))\}\,. \tag{27}$$

In analogy to Eq. (21), the ensemble average can be factored into three terms: one describing a collision of duration τ_d centered around $t=0$, a second similar term describing a collision centered around t, and the usual term which embodies the broadening and shifting effects of completed collisions. As a consequence, for $t \gg \tau_d$, Eq. (27) can be written in the form

$$C_3^{II}(t) = n^2P(J)|m|(p^A_{JJ'})^2 e^{i\omega_{J'J}t - \Gamma'_{J'J}t/2} \times\left(\Delta_{J'J}4\pi\int_0^\infty p(R)g(R)R^2\,dR\right)^2, \tag{28}$$

and the corresponding line shape function becomes

$$\phi^{II}(\omega) = n^2P(J)|m|(p^A_{JJ'})^2\left(4\pi\int_0^\infty p(R)g(R)R^2\,dR\right)^2 \times\left(\frac{(\Delta'^2_{J'J}-\Delta''^2_{J'J})\Gamma'_{J'J}/2\pi}{(\frac{1}{2}\Gamma'_{J'J})^2+(\omega-\omega_{J'J})^2} + \frac{2\Delta'_{J'J}\Delta''_{J'J}(\omega-\omega_{J'J})/\pi}{(\frac{1}{2}\Gamma'_{J'J})^2+(\omega-\omega_{J'J})^2}\right). \tag{29}$$

Again, because of the limitations of the impact approximations, the intensity obtained by integrating (29) is not correct; the proper value can be obtained through Eq. (27) by setting $t=0$, and it is in agreement with that derived previously.[9] One should use Eq. (29), however, when comparing with the experimental data as will be discussed in Sec. VI.

VI. DISCUSSION AND COMPARISON WITH EXPERIMENT

Using the results of Secs. III–V, including the contributions from the pure allowed dipole, the interference between the allowed and the induced dipoles, and the pure induced dipole interference, the total absorption coefficient per unit wavelength for the sharp R and P lines can be written

$$\alpha(\omega)=n\left(\frac{4\pi^2}{3\hbar c}\right)\omega P(J)|m|(p^4_{JJ'})^2\left(\frac{\Gamma'_{J'J}/2\pi}{(\frac{1}{2}\Gamma'_{J'J})^2+(\omega-\omega_{J'J})^2}[1+2n\Delta' I+n^2(\Delta'^2-\Delta''^2)I^2]\right.$$
$$\left.+\frac{2(\omega-\omega_{J'J})/\pi}{(\frac{1}{2}\Gamma'_{J'J})^2+(\omega-\omega_{J'J})^2}(n\Delta''_{J'J}I+n^2\Delta'_{J'J}\Delta''_{J'J}I^2)\right) \tag{30}$$

where

$$I=4\pi\int_0^\infty p(R)g(R)R^2\,dR\,.$$

Before comparing this expression with the experimental data, it is of interest to consider in more detail the complex quantity $\Delta_{J'J}$ which appears in the line shape. Using Eqs. (23) and (24), this can be written in terms of averages over single collisions

$$\Delta_{J'J}=\frac{\langle\langle if|\{p(R(t))U_i(\tau_d)U_f^\dagger(\tau_d)\}|if\rangle\rangle}{\{p(R)\}}\,. \tag{31}$$

In principle, Δ can be calculated from a knowledge of the interaction between two colliding molecules, although in practice, this would be a difficult calculation. Some insight, however, can be obtained from the form of Eq. (31). In view of the unitarity of the time-development operators, the absolute magnitude of either Δ' or Δ'' can never exceed unity. As collisions increase in disruptive effect, Δ becomes complex and Δ' decreases from its unperturbed value of unity. One can thus envision several limiting cases.

(i) *Gentle-encounter limit.* In this case, the time-development operators remain real and essentially equal to unity; i.e., $\Delta\simeq 1$. The corresponding line shape would be a pressure-broadened and -shifted Lorentzian with intensity in agreement with that of Ref. 9.

(ii) *Violent-encounter limit.* Here, through either collision-induced inelastic transitions or large random phase shifts, the U's would differ substantially from unity and, in general, give rise to a near-zero value for Δ. In this case the line shape would again approach a symmetric Lorentzian, while the corresponding intensity would approach that of an allowed line.

(iii) *Phase-shift limit.* In some cases, the primary influence of the time-development operators may be described by phase shifts introduced into the initial and final states during adiabatic collisions. The ensemble averaging over dynamical variables can then be carried out in a way analogous to that employed in the calculation of pressure broadening and shifting.[11] The resultant Δ can thus be approximated as

$$\Delta\simeq\frac{\int_0^\infty vf(v)dv\,b\,db\int_{-\infty}^\infty p(t)\exp[i\int_{-\infty}^t[\omega_{fi}(t')-\omega^0_{fi}]dt']dt}{\int_0^\infty vf(v)dv\,b\,db\int_{-\infty}^\infty p(t)dt}\,, \tag{32}$$

where $f(v)$ is the Maxwell distribution of speeds v, and b is the impact parameter.[11] The numerical evaluation of these integrals with realistic potentials and induced dipoles is beyond the scope of the present paper, however.

We now turn to the comparison of the present theory with the detailed experimental results of McKellar[2] on the fundamental band of HD. He found that the R and P lines can be represented by a line shape of the form

$$\frac{\alpha(\omega)}{n\omega}=\frac{D_0\Gamma\pi}{2}\left((1-q^{-2})\frac{\Gamma/2\pi}{(\frac{1}{2}\Gamma)^2+(\omega-\omega_0)^2}\right.$$
$$\left.+q^{-1}\frac{2(\omega-\omega_0)/\pi}{(\frac{1}{2}\Gamma)^2+(\omega-\omega_0)^2}\right)\,, \tag{33}$$

where D_0, Γ, q, and ω_0 are density-dependent fitting parameters. Actually, (33) differs by a frequency-independent quantity from the expression used by McKellar; this of course does not influence the value of the parameters listed above. Expression (33) is of the same form as the theoretical line shape (30), and by identification we therefore have

$$\tfrac{1}{2}D_0\Gamma\pi(1-q^{-2})$$
$$=\tilde\alpha_1(n)=\tilde\alpha_1(0)[1+2n\Delta' I+n^2(\Delta'^2-\Delta''^2)I^2] \tag{34}$$

and

$$\tfrac{1}{2}D_0\Gamma\pi q^{-1}=\tilde\alpha_1(0)(n\Delta'' I+n^2\Delta'\Delta'' I^2) \tag{35}$$

where

$$\tilde{\alpha}_1(n) = \int \frac{\alpha(\omega)}{n\omega} d\omega \ ,$$

and where the subscripts $J'J$ on Δ have been suppressed. Note that

$$\tilde{\alpha}_1(0) \equiv (4\pi^2/3\hbar c) P(J) |m| (p^{\mathbf{A}}_{J'J})^2$$

represents the pure allowed dipole intensity.

Experimental values of $\tilde{\alpha}_1(n)$ for the $R_1(0)$ line at 77 K for a number of densities have been given in Ref. 8 and are reproduced in Fig. 1. Similarly, we give in Fig. 2 the corresponding experimental values of q^{-1} taken from Ref. 2. By combining (34) and (35), we have, up to terms of order n^3

$$q^{-1} = n\Delta''I/(1 + n\Delta'I) . \tag{36}$$

The theoretical expression for $\tilde{\alpha}_1(n)$ and q^{-1} contain the two density-independent parameters $\Delta'I$ and $\Delta''I$. If the theory adequately represents the experimental results, it should be possible to fit the data in Figs. 1 and 2 with reasonable values of $\Delta'I$ and $\Delta''I$. This is indeed the case, and in Figs. 1 and 2, the solid curves represent the theoretical results for $\Delta'I = -5.5 \times 10^{-3}$ and $\Delta''I = -4 \times 10^{-3}$. The integral I was calculated previously[8] where it was found that $I \simeq -7 \times 10^{-3}$ and, therefore, $\Delta' \simeq 0.8$ and $\Delta'' \simeq 0.6$, respectively. These values of Δ' and Δ'' satisfy the unitarity condition, and the fact that Δ' is still close to unity, suggests that a theoretical calculation of Δ can be performed within the phase-shift formalism discussed above.

The contribution to the interference by the pure induced dipoles is relatively small and it would therefore be of interest to investigate the region of higher density where this effect is more important. This applies in particular to the line-shape factor q^{-1}, which is more sensitive to an increase in the density than $\tilde{\alpha}_1(n)$. In addition, it is expected that the asymmetry of the profile will be more pronounced at higher temperatures. While the analysis discussed above applied specifically to the $R_1(0)$ line, similar interference effects occur in other lines of the fundamental band,[2] and in the pure rotational spectrum as well.[8]

Before concluding, there are two additional experimental findings on which we would like to comment. First, the $R(0)$ line in the first overtone band (the only line in this band reported) did not show appreciable asymmetry.[2] This is consistent with the present results in that the overlap-induced dipole in H_2 which gives rise to the component in HD which interferes [cf. Eq. (18)] is known to be small for this transition.[15] The interference and concomitant Fano line shape would only become apparent at higher densities. Second, the asymmetry of the $P(1)$ line in the fundamental was shaded in the opposite direction to that of the $R(J)$ lines.[2] This implies that Δ'' has the opposite sign for this line than that found for $R(0)$. As mentioned above, in some cases it should be possible to calculate Δ using a phase-shift approach. It is well known that for calculations of the pressure-induced line shifts, the phase shifts associated with the $R(0)$ and $P(1)$ lines have the opposite

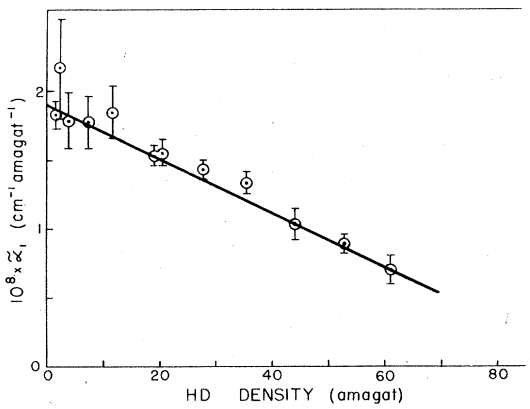

FIG. 1. Experimental values for the integrated intensity of the fundamental $R_1(0)$ line of pure HD measured at various densities at 77 K; the solid curve is the theoretical fit [Eq. (34)] for the parameters $\Delta'I = -5.5 \times 10^{-3}$ and $\Delta''I = -4 \times 10^{-3}$.

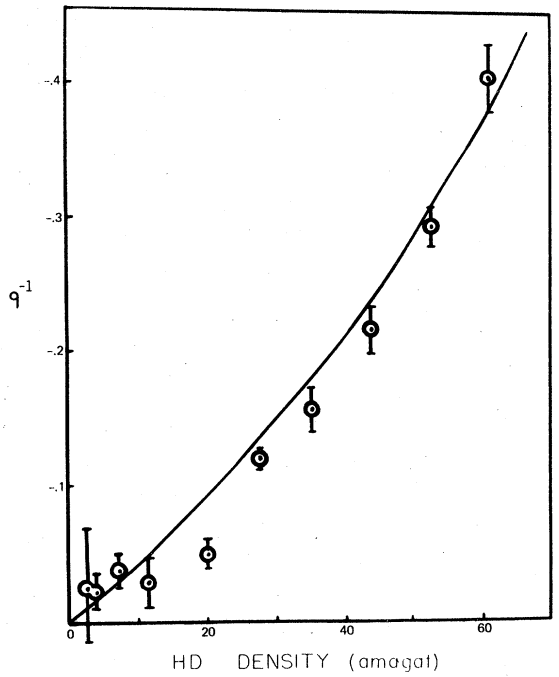

FIG. 2. Experimental values for the line-shape parameter of the $R_1(0)$ line at 77 K; the solid curve is the theoretical fit [Eq. (36)] for the parameters $\Delta'I = -5.5 \times 10^{-3}$ and $\Delta''I = -4 \times 10^{-3}$.

sign.[11] This results from the fact that in addition to the average (first-order perturbation) shift which is the same for both lines, there is a large second-order contribution which is nonzero for these lines only, and which has the opposite sign for the $R(0)$ and $P(1)$ lines. In the present case for the calculation of Δ, the short-range second-order shift would be expected to dominate since the induced dipole $p(R)$, is itself a peaked short-range function. It would, therefore, be of interest to determine whether the shading of the $P(2)$ asymmetry is the same as the R lines as expected from the above considerations.

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[1]R. A. Durie and G. Herzberg, Can. J. Phys. 38, 806 (1960).
[2]A. R. W. McKellar, Can. J. Phys. 51, 389 (1973).
[3]A. R. W. McKellar, Can. J. Phys. 52, 1144 (1974).
[4]J. Bejar and H. P. Gush, Can. J. Phys. 52, 1669 (1974).
[5]R. D. G. Prasad and S. P. Reddy, J. Chem. Phys. 62, 3582 (1975); 65, 83 (1976); 66, 707 (1977); 66, 5259 (1977).
[6]N. H. Rich and A. R. W. Mckellar, Can. J. Phys. 54, 486 (1976).
[7]J. D. Poll, R. H. Tipping, R. D. G. Prasad, and S. P. Reddy, Phys. Rev. Lett. 36, 248 (1976).
[8]R. H. Tipping, J. D. Poll, and A. R. W. McKellar, Can. J. Phys. 56, 75 (1978).
[9]R. M. Herman, Phys. Rev. Lett. 42, 1206 (1979).
[10]H. R. Griem, *Plasma Spectroscopy* (McGraw-Hill, New York, 1964).
[11]R. H. Tipping and R. M. Herman, J. Quant. Spectrosc. Radiat. Transfer 10 881 (1970); R. M. Herman and R. H. Tipping, *ibid*, 10, 897 (1970).
[12]E. W. Smith, C. R. Vidal, and J. Cooper, J. Res. Natl. Bur. Stand. A 73, 389 (1969).
[13]M. Baranger, Phys. Rev. 111, 494 (1958); 112, 855 (1958).
[14]J. C. Lewis and J. Van Kranendonk, Can. J. Phys. 50, 352 (1972); J. C. Lewis, *ibid*. 50, 2881 (1972).
[15]A. R. W. McKellar and H. L. Welsh, Proc. R. Soc. A 322, 421 (1971).